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(54) Title: COMPOSITIONS OF STYRENIC BLOCK COPOLYMER RESIN AND POLYPHENYLENE ETHER RESIN		
(57) Abstract The invention generally relates to novel compositions comprising (i) a styrenic block copolymer, and (ii) at least one polyphenylene ether resin having an intrinsic viscosity within the range of about 0.05 dl/g to about 0.60 dl/g, preferably within the range of about 0.08 dl/g to about 0.20 dl/g, more preferably within the range of about 0.08 dl/g to about 0.15 dl/g, as measured in chloroform at 25 °C. In a preferred embodiment, the compositions are substantially free of other thermoplastic resins. The invention also relates to processes to manufacture the blends as well as articles made from the blends.		

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COMPOSITIONS OF STYRENIC BLOCK COPOLYMER RESIN AND POLYPHENYLENE ETHER
RESIN

CROSS-REFERENCE TO RELATED APPLICATIONS

Not Applicable

FEDERALLY SPONSORED RESEARCH

Not Applicable

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention generally relates to novel compositions comprising (i) a styrenic block copolymer, and (ii) at least one polyphenylene ether resin having an intrinsic viscosity within the range of about 0.05 dl/g to about 0.60 dl/g, preferably within the range of about 0.08 dl/g to about 0.20 dl/g, more preferably within the range of about 0.08 dl/g to about 0.15 dl/g, as measured in chloroform at 25°C. In a preferred embodiment, the compositions are substantially free of other thermoplastic resins.

The invention also relates to processes to manufacture the blends as well articles made from the blends.

2. Brief Description of the Related Art

Polyphenylene ether resins (hereinafter "PPE") are commercially attractive materials because of their unique combination of physical, chemical, and electrical properties. It is known in the art that forming compositions with other polymers can materially alter the properties of the PPE and many such PPE compositions have been disclosed in the prior art.

Blends of PPE and styrenic block copolymer are of great interest because PPE can potentially add improved temperature resistance and dimensional stability to styrenic block copolymer. However, such blends very often suffer from limitations of their own, apart from the limitations of the individual resins, due to the relative high molecular weight and concomitant high melt viscosity of commercially available PPE of art. Accordingly, the beneficial property aspects which one resin could possibly confer on the other may not be fully realized.

In large part due to the deficiencies of the current state of the PPE art, commercialization of PPE- styrenic block copolymer compositions has been limited. It is therefore apparent that a need continues to exist for the development of compositions of PPE and styrenic block copolymer as well as for methods to manufacture such compositions.

SUMMARY OF THE INVENTION

The needs discussed above have been generally satisfied by the discovery of a novel compositions comprising (i) at least one styrenic block copolymer, and (ii) at least one PPE having an intrinsic viscosity within the range of about 0.05 dl/g to about 0.60 dl/g, preferably within the range of about 0.08 dl/g to about 0.20 dl/g, more preferably within the range of about 0.08 dl/g to about 0.15 dl/g, as measured in chloroform at 25°C.

The PPE is preferably prepared by a process comprising oxidative coupling in a reaction solution at least one monovalent phenol species using an oxygen containing gas and a complex metal catalyst to produce a PPE having an intrinsic viscosity within the range of about 0.05 dl/g to about 0.60 dl/g, preferably within the range of about 0.08 dl/g to about 0.20 dl/g, more preferably within the range of about 0.08 dl/g to about 0.15 dl/g, as measured in chloroform at 25°C; removing at least a portion of the complex metal catalyst with an aqueous containing solution; and isolating the PPE through devolatilization of the reaction solvent.

The description that follows provides further details regarding various embodiments of the invention.

DESCRIPTION OF THE DRAWINGS

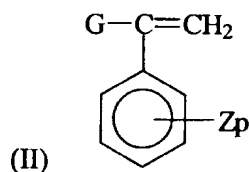
Not applicable

DETAILED DESCRIPTION OF THE INVENTION

The term "styrenic block copolymer" is used herein to indicate polymers having a poly(alkenylaromatic) block of at least about 15 repeat units attached to a second polymer or copolymer of at least about 15 repeat units. The styrenic block copolymers can generically be represented by the general formula (I):



wherein "styrene" is an alkenylaromatic monomer of the formula (II):



wherein G is hydrogen, lower alkyl or halogen; Z is vinyl, halogen or lower alkyl; and p is from 0 to 5, and wherein X is a second polymer or copolymer of one or more monomers, n is at least 15, preferably at least 20, and m is at least 1 and can vary to 5 or more. The chemical nature of X can vary widely and include, for example, polyesters, polyamides, polyolefins, polycarbonates, polyimides, polysulfones, polyethersulfones, polyphenylene ethers, liquid crystalline polymers, as well as copolymers containing at least one of the foregoing, and the like.

The term "styrenic block copolymer" includes a variety of structures, including block and graft copolymers, and can be of a variety of architectures, including di-block, tri-block, or higher multi-block, branched, multi-arm, radial.

comb, and tapered as well as combination of the foregoing. The general formula (I) above is intended to include all the foregoing structures provided that each contains at least one poly(alkenylaromatic) block and at least one second polymer block. The block sizes may also vary within the copolymers, provided that there is at least one styrenic block of at least about 15 repeat units or more.

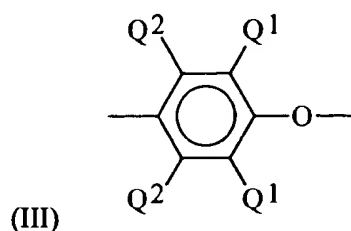
In a preferred embodiment of the invention, the styrenic block copolymer is an olefinic copolymer with at least one poly(alkenylaromatic) block, preferably derived from styrene. Especially preferred are the so-called elastomeric block copolymers, for example, A-B-A triblock copolymers and A-B diblock copolymers wherein A is a poly(alkenylaromatic) block and B is an elastomer block, as well as mixtures including the foregoing. These A-B and A-B-A type block copolymers are thermoplastic rubbers comprised of a rubber block, e.g., a butadiene block that may be partially or totally hydrogenated.

Included A-B and A-B-A type block copolymers are disclosed in, for example, U.S. Patent Nos. 3,078,254, 3,402,159, 3,297,793, 3,265,765, and 3,594,452, 5,149,741, and 5,847,051, and U.K. Patent 1,264,741. Examples of typical species of A-B and A-B-A block copolymers include polystyrene-polybutadiene (SBR), polystyrene-poly(ethylene-propylene), polystyrene-polyisoprene, polystyrene-poly(ethylene-butylene), poly(α -methylstyrene)-polybutadiene, polystyrene-polybutadiene-polystyrene (SBR), polystyrene-poly(ethylene-butylene)-polystyrene, polystyrene-polyisoprene-polystyrene and poly(α -methylstyrene)-polybutadiene-poly(α -methylstyrene), as well as the selectively hydrogenated versions thereof. Mixtures containing at least one of the aforementioned block copolymers are also useful. The styrenic block copolymer may also contain at least one functional group such that the styrenic block copolymer is a functionalized styrenic block copolymer. The functional group is generally at least one moiety of the group consisting of anhydride, amino, hydroxyl, epoxy, oxazoline, and orthoester.

A wide variety of useful A-B and A-B-A block copolymers are available commercially from a number of sources, including Phillips Petroleum under the trademark SOLPRENE, Shell Chemical Co., under the trademark KRATON, Dexco under the tradename VECTOR, and Kuraray under the trademark SEPTON.

In one embodiment, the compositions containing the styrenic block copolymer also contains an elastomeric polyolefin, for example, an ethylene-propylene rubber or an ethylene-propylene-diene elastomer. In an embodiment, the essential structural units of the elastomeric polyolefin are derived from ethylene and at least one C₃₋₈ 1-olefin, such as, propylene, 1-butene, 1-hexene, and 1-octene. The proportions of ethylene and at least one C₃₋₈ 1-olefin are not critical provided that they together constitute the major portion of the polymer. The diene portion is at least one non-conjugated diene, such as ethylidene norbornene, 1,4-hexadiene, or dicyclopentadiene. These elastomeric polyolefins are known in the art as EPR and EPDM elastomers. The compositions may also include at least one functionalized elastomeric polyolefin, either with or without the elastomeric polyolefin, although it should be noted that functionalized elastomeric polyolefins generally contain at least a measurable amount of non-functionalized elastomeric polyolefin. The functional group is generally at least one moiety of the group consisting of anhydride, amino, hydroxyl, epoxy, oxazoline, and orthoester. Methods to prepare such functionalized elastomeric polyolefins are known in the art and include use of a compound containing a carbon-carbon double bond in addition to one of the aforementioned functional groups to afford the functionality onto the elastomeric polyolefin.

The PPE employed in the present invention are known polymers comprising a plurality of structural units of the formula (III):



wherein each structural unit may be the same or different, and in each structural unit, each Q^1 is independently halogen, primary or secondary lower alkyl (i.e., alkyl containing up to 7 carbon atoms), phenyl, haloalkyl, aminoalkyl, hydrocarbonoxy, or halohydrocarbonoxy wherein at least two carbon atoms separate the halogen and oxygen atoms; and each Q^2 is independently hydrogen, halogen, primary or secondary lower alkyl, phenyl, haloalkyl, hydrocarbonoxy or halohydrocarbonoxy as defined for Q^1 . Most often, each Q^1 is alkyl or phenyl, especially C_{1-4} alkyl, and each Q^2 is hydrogen.

Both homopolymer and copolymer PPE are included. The preferred homopolymers are those containing 2,6-dimethyl-1,4-phenylene ether units. Suitable copolymers include random copolymers containing such units in combination with (for example) 2,3,6-trimethyl-1,4-phenylene ether units. Also included are PPE containing moieties prepared by grafting vinyl monomers or polymers such as polystyrenes and elastomers, as well as coupled PPE in which coupling agents such as low molecular weight polycarbonates, quinones, heterocycles and formals undergo reaction in known manner with the hydroxy groups of two poly(phenylene ether) chains to produce a higher molecular weight polymer, provided a substantial proportion of free OH groups remains. Also included are PPE 's containing a functional endgroup, obtained, for example, from reaction with a reactive compound having the functional endgroup.

The intrinsic viscosity (hereinafter "I.V.") of the PPE is most often in the range of about 0.05-0.60 dl./g., preferably about 0.08-0.20 dl./g., more preferably in the range of about 0.10-0.15 dl./g., as measured in chloroform at 25°C. As the I.V., a

measure of molecular weight, decreases the physical properties of the compositions becomes enhanced in many ways. For example, compositions wherein the PPE has an I.V. in the range of about 0.10-0.15 dl./g., typically exhibit a higher heat resistance than compositions wherein the PPE has an I.V. substantially higher (e.g., an I.V. of greater than about 0.38 dl/g) than this range. Although not wishing to be bound by any theory, it is thought that the solubility of the PPE in the styrenic block copolymer has increased as the molecular weight, as indicated by I.V., has decreased. Additionally, because of improved viscosity matching, a more uniform dispersion would be obtained which would contribute to enhanced physical properties. It has been shown that PPE with a low I.V. offers improvements in flame retardance performance as correlated with faster rates of char formation. Preferred low molecular weight PPE include generally those that have a number average molecular weight within the range of about 1250 to about 7000 and a weight average molecular weight within the range of about 2500 to about 15,000, as determined by gel permeation chromatography, with a preferred number average molecular weight within the range of about 1750 to about 4000 and a weight average molecular weight within the range of about 3500 to about 9,000, as determined by gel permeation chromatography. Correlation of glass transition temperatures (T_g) to molecular weight is particular to PPE structures. For illustration, the T_g for poly(2,6-dimethylphenylene ether) resin unexpectedly drops about 35% for ten fold drop in molecular weight. Accordingly, the retention of heat properties is better than would be expected for a given I.V. and affords an unexpected benefit for applications where high flow and retention of heat resistance is important.

The PPE are typically prepared by the oxidative coupling of at least one monohydroxyaromatic compound such as 2,6-xilenol, 2,3,6-trimethylphenol, or mixtures of the foregoing. Catalyst systems are generally employed for such coupling and they typically contain at least one heavy metal compound such as a copper, manganese, or cobalt compound, usually in combination with various other materials.

It will be apparent to those skilled in the art from the foregoing that the PPE contemplated in the present invention include all those presently known, irrespective of variations in structural units or ancillary chemical features.

The polymerization of the phenolic monomer may be carried out by adding the phenolic monomer or monomers to a suitable reaction solvent and preferably, a copper-amine catalyst. It is preferred to carry out the polymerization in the presence of a cupric or cuprous salt-secondary amine catalyst such as, for example, cupric chloride and di-n-butylamine. The polymerizations are advantageously carried out in the presence of an inorganic alkali metal bromide or an alkaline earth metal bromide. The inorganic bromides may be used at a level of from about 0.1 mole to about 150 moles per 100 moles of phenolic monomer. These catalyst materials are described in U.S. Pat. No. 3,733,299 (Cooper et al.). Tetraalkylammonium salts may also be employed as promoters if desired. These promoters are disclosed in U.S. Pat. No. 3,988,297 (Bennett et al.).

The primary, secondary or tertiary amine component of the catalyst complex generally correspond to those disclosed in U.S. Pat. Nos. 3,306,874 and 3,306,875 (Hay). Illustrative members include aliphatic amines, including aliphatic mono- and di-amines, where the aliphatic group can be straight or branched chain hydrocarbon or cycloaliphatic. Preferred are aliphatic primary, secondary and tertiary monoamines and tertiary diamines. Especially preferred are mono-, di- and tri(lower) alkyl amines, the alkyl groups having from 1 to 6 carbon atoms. Typically, there can be used mono-, di- and tri-methyl, ethyl, n-propyl i-propyl, n-butyl substituted amines, mono- and di-cyclohexylamine, ethylmethyl amine, morpholine, N-(lower) alkyl cycloaliphatic amines, such as N-methylcyclohexylamine, N,N'-dialkylethylenediamines, the N,N'-dialkylpropanediamines, the N,N,N',-trialkylpentanediamines, and the like. In addition, cyclic tertiary amines, such as pyridine, alpha-collidine, gamma picoline, and the like, can be used. Especially useful are N,N,N',N'-tetraalkylethylenediamines, butane-diamines, and the like.

Mixtures of such primary, secondary and tertiary amines may be used. A preferred mono alkyl amine is n-butyl amine; a preferred dialkyl amine is di-n-butyl amine; and a preferred trialkyl amine is triethylamine. A preferred cyclic tertiary amine is pyridine. The concentration of primary and secondary amine in the reaction mixture may vary within wide limits, but is desirably added in low concentrations. A preferred range of non-tertiary amines comprises from about 2.0 to about 25.0 moles per 100 moles of monovalent phenol. In the case of a tertiary amine, the preferred range is considerably broader, and comprises from about 0.2 to about 1500 moles per 100 moles of monovalent phenol. With tertiary amines, if water is not removed from the reaction mixture, it is preferred to use from about 500 to about 1500 moles of amine per 100 moles of phenol. If water is removed from the reaction, then only about 10 moles of tertiary amine, e.g., triethylamine or triethylamine, per 100 moles of phenol need be used as a lower limit. Even smaller amounts of tertiary diamines, such as N,N,N',N'-tetramethylbutanediamine can be used, down to as low as about 0.2 mole per 100 moles of phenol.

One unexpected advantage in using PPE having an I.V. in the range of about 0.08 to about 0.20 dl/g is that the level of amine incorporation is relatively low when made by the methods as described herein. For example, when using dibutylamine (DBA) in the polymerization process, the level of DBA incorporated into high molecular weight (e.g., 0.48 I.V.) PPE is generally between about 0.9 to about 1.0% by weight based on the weight of the PPE. Conversely, the level of DBA incorporated into low molecular weight (e.g., 0.11 I.V.) PPE is generally between about 0.15 to about 0.28% by weight based on the weight of the PPE. It is desirable to have the amine level very low on the PPE to minimize the amount that becomes thermally liberated during subsequent processing and can adversely affect properties of the composition as well as taste and odor. Thus, the present invention includes compositions of at least one styrenic block copolymer and a PPE having an incorporated amine level of less than about 0.3% by weight based on the weight of the PPE.

The low IV PPE has a higher degree of branching than PPE resins that have a higher IV and that are produced via the conventional isolation process utilizing an anti-solvent. The branching is visible in the form of phenyl methylene ether bonds detected by NMR that are not detected in high molecular weight PPE (i.e. having an I.V. greater than about 0.3 dl/g). The branching is also indicated by the increased melt flow and molecular weight distribution of low I.V. PPE. Also included in the present invention are compositions of at least one styrenic block copolymer and a low I.V. PPE having enhanced branching as compared to high molecular weight PPE.

Typical examples of cuprous salts and cupric salts suitable for the process are shown in the Hay patents. These salts include, for example, cuprous chloride, cuprous bromide, cuprous sulfate, cuprous azide, cuprous tetramine sulfate, cuprous acetate, cuprous butyrate, cuprous toluate, cupric chloride, cupric bromide, cupric sulfate, cupric azide, cupric tetramine sulfate, cupric acetate, cupric butyrate, cupric toluate, and the like. Preferred cuprous and cupric salts include the halides, alkanoates or sulfates, e.g., cuprous bromide and cuprous chloride, cupric bromide and cupric chloride, cupric sulfate, cupric fluoride, cuprous acetate and cupric acetate. With primary and secondary amines, the concentration of the copper salts is desirable maintained low and preferably varies from about 0.2 to 2.5 moles per 100 moles of monovalent phenol. With tertiary amines, the copper salt is preferably used in an amount providing from about 0.2 to about 15 moles per 100 moles of the monovalent phenol.

Cupric halides are generally preferred over cuprous halides for the preparation of the copper amine catalyst because of their lower cost. The use of the copper (I) species also greatly increases the rate of oxygen utilization in the early stages of the polymerization reaction and the lower oxygen concentration in the head space of the reactor helps in reducing the risk of fire or explosion in the reactor. A process for the preparation and use of suitable copper-amine catalysts is in U.S. Pat. No. 3,900,445 (Cooper et al.).

A faster initial reaction rate with the copper (I) based catalyst also results in less accumulation of unreacted monomer and a reduction in the amount of undesirable tetramethyldiphenylquinone produced. The tetramethyldiphenylquinone, a backward dimer, is believed to incorporate into the PPE through equilibration reactions. The equilibration reactions lead to a drop in the intrinsic viscosity of the PPE due to the decrease in molecular weight of the PPE from the incorporation of the dimer. Minimization of the tetramethyldiphenylquinone during the oxidation coupling is desirable so as to avoid the drop in molecular weight and the accompanying difficulties in having to build to a higher than desired molecular weight to offset the loss during equilibration of the backward dimer. Additionally, by minimizing the amount of tetramethyldiphenylquinone formed and consequently minimizing the amount of tetramethyldiphenylquinone incorporated into the backbone of the PPE, a PPE polymer change that is predominantly hydroxyl monofunctional is possible. By "hydroxyl monofunctional" is meant that one end of the polymer chain, i.e. the "head end", is a 2,6-dimethyl phenol with the polymer chain extending from the 4-position. The other end, i.e. the "tail end", has the hydroxyl on the 2,6-dimethyl phenol connected into the polymer and hence is non-functional. In a preferred embodiment, the utilized PPE is at least 70%, preferably at least 85%, most preferably, at least 95% by weight hydroxyl monofunctional. Additionally, in another preferred embodiment, the utilized PPE had in the reaction mixture less than a 10% drop, preferably less than a 5% drop, most preferably less than a 3% drop in I.V. during an equilibration step after the oxidative polymerization of the phenolic monomers. However, changing the reaction conditions can affect the amount of TMDQ formed and equilibrated into the PPE. This in turn can change the structure of the PPE and the amount of, for example, bi-functional chains. From the foregoing, it should be clear that preferred PPE include low molecular weight PPE having number average molecular weights from about 1,000 to 10,000 g/mol or weight average molecular weights from about 3,000 to 35,000 g/mol. In addition, it is advantageous for the PPE have low levels of bound amine functionality, and a high level of chains containing only one hydroxyl

groups. Illustrative of the preferred embodiments of the present invention are the PPEs of the following examples.

amine, monofunctional resins (PPE-1 and PPE-2), and their physical properties are shown in Table 1 in comparison to a higher molecular weight commercial PPE (PPE-3 below).

Table 1

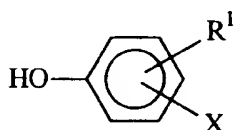
	PPE-1	PPE-2	PPE-3
<i>Property:</i>			
% Chains having 2 OH groups per molecule (Bifunctional Chains)	9.3	12.2	82.6
Hydroxyl endgroup Concentration ($\mu\text{mol/g}$)	464.6	366.5	120.3
Intrinsic Viscosity (dl/g)	0.12	0.15	0.40
Absolute M_n (g/mol)	2,331	3,081	12,500
M_n (g/mol)	2,197	3,114	15,399
M_w (g/mol)	7,882	11,007	39,868
M_z (g/mol)	13,297	18,682	70,489
M_w/M_n	3.58	3.53	2.58
Tg (DSC, $^{\circ}\text{C}$)	166.0	176.3	212.0

One advantage of the formation of tetramethyldiphenylquinone during the reaction process is that it affords the possibility to redistribute various compounds into the PPE. Through redistribution, a wide range of functionalized phenolic

compounds can be introduced to afford an equally wide range of functionalized PPE. For example, after the end of the oxidative coupling reaction as determined by the desired molecular weight of the PPE, at least one phenolic compound may be added to the reaction mixture and allowed to circulate while maintaining the temperature preferably between about 20° and about 150°C, preferably between about 60° and 80°C. The reaction mixture is maintained at temperature for about 30 to about 90 minutes, although longer times are possible. During this redistribution step, the flow of oxygen has been preferably halted as the oxidative coupling has been completed. Generally, higher redistribution conversions are obtained under air as opposed to nitrogen.

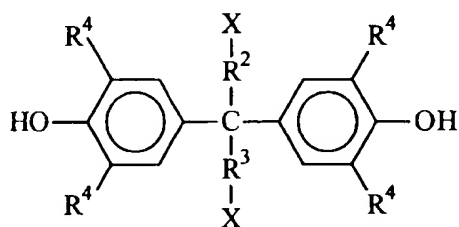
The functionalized phenolic compound may be chosen from the following illustrative list:

A) phenolic compounds with formula



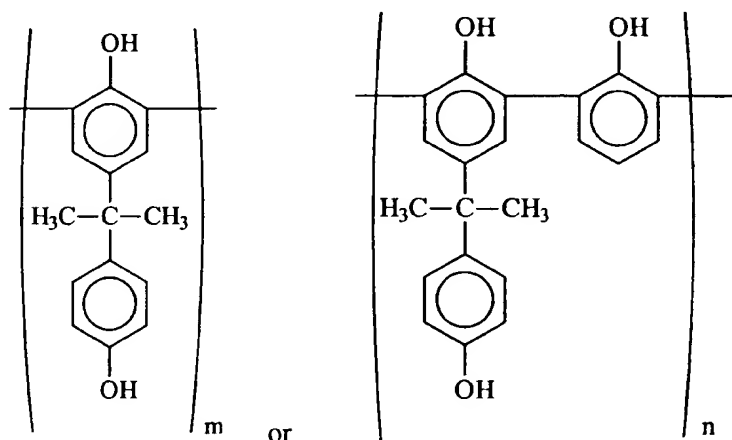
wherein R¹ represents a hydrogen-atom or an alkyl group and X represents an allyl group, an amino group, a protected amino group (e.g., protected by a tertiary-butyl carbonate), a carboxyl group, a hydroxy group, an ester group or a thiol group, wherein R¹ is an alkyl group when X represents a hydroxy group or an ester group, wherein X may be separated from the phenol ring through an alkyl group and wherein the total number of carbon atoms in the alkyl groups attached to the phenol ring is not more than six;

B) bisphenol compounds with formula



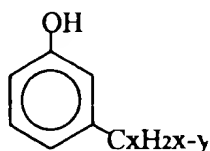
wherein each X, independently of the other X represents a hydrogen atom, an allyl group, an amino group, a protected amino group (e.g., protected by a tertiary-butyl carbonate), a carboxyl group, a hydroxy group, an ester group or a thiol group, with the proviso that not more than one X group represents a hydrogen atom, R^2 and R^3 represent an hydrogen atom or an alkyl group with 1-6 carbon atoms and each R^4 represents independently of the other R^4 a hydrogen atom, a methyl group or an ethyl group;

C) a phenolic compound with at least one of the formulas:



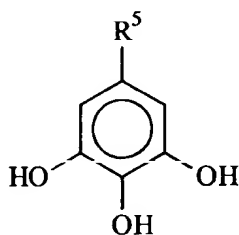
wherein m and n have values from 2-20;

D) phenolic compounds with formula



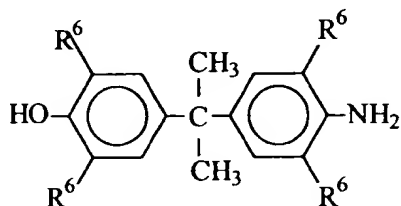
wherein x has a value of 12-20 and y has a value of 1-7 or a derivative thereof;

E) multifunctional phenolic compounds with formula



wherein R⁵ represents a hydrogen atom, an alkyl group, an allyl group, an amino group, a protected amino group (e.g., protected by a tert-butyl carbonate), a carboxyl group, a hydroxy group, an ester group or a thiol group; or

F) phenolic compounds with amino groups with formula



wherein R⁶ represents independently of one another a hydrogen atom, an alkyl group or a methylene phenol group.

At the end of the redistribution, the functionalized PPE has a lower intrinsic viscosity, and hence a lower molecular weight, than does the PPE at the end of the oxidative coupling reaction. The degree of the decrease is determined at least in part by the amount of phenolic compound utilized and the amount of catalyst, e.g.,

PPE has a weight average molecular weight of at least 1000, preferably between about 3000 and about 70,000 as compared to polystyrene standards. In another preferred embodiment, the functionalized PPE has an intrinsic viscosity of between about 0.05 dl/g and 0.50 dl/g, preferably between about 0.08 dl/g and 0.30 dl/g, more preferably between about 0.08 dl/g and about 0.15 dl/g as measured in chloroform at 30°C. The PPE may have a bi-modal distribution of molecular weights.

It should be clear that the present invention also includes reaction products between the PPE and styrenic block copolymer. Such reaction products include, but are not limited to, random copolymers of PPE and the styrenic block copolymer and block copolymers of PPE and the styrenic block copolymer as well as variations of the foregoing. It is thought that even low levels of the copolymers can improve the compatibility between the resins. Improved compatibility can reduce delamination tendencies and improve the physical properties of the compositions. Also included in the present invention are compositions comprising PPE, the styrenic block copolymer, and copolymers of PPE and at least one elastomeric polyolefin.

The polymerization reaction is preferably performed in a solvent. Suitable solvents are disclosed in the above-noted Hay patents. Aromatic solvents such as benzene, toluene, ethylbenzene, xylene, and o-dichlorobenzene are especially preferred, although tetrachloromethane, trichloromethane, dichloromethane, 1,2-dichloroethane and trichloroethylene may also be used. The weight ratio between solvent and monomer is normally in the range from 1:1 to 20:1, ie. up to a maximum 20-fold excess of solvent. The ratio between solvent and monomer is preferably in the range from 1:1 to 10:1 by weight.

The process and reaction conditions for the polymerization, such as reaction time, temperature, oxygen flow rate and the like are modified based on the exact target molecular weight desired. The endpoint of the polymerization is conveniently determined with an in-line viscosity meter. Although other methods such as making molecular weight measurements, running to a predetermined reaction time,

controlling to a specified endgroup concentration, or the oxygen concentration in solution may also be utilized.

The temperature to carry out the polymerization stage of the invention generally ranges from about 0°C. to about 95°C. More preferably, the temperature range is from about 35°C. to about 45°C with the higher reaction temperature near the end of reaction. At substantially higher temperatures, side reactions can occur leading to reaction by-products and at temperatures substantially lower, ice crystals form in the solution.

Many diverse extractants or chelating agents may be used in the practice of the invention to complex with the catalyst after the end of the polymerization reaction. For example, sulfuric acid, acetic acid, ammonium salts, bisulfate salts and various chelating agents may be used. When these materials are added to a PPE reaction solution, the copper-amine catalyst becomes poisoned and further oxidation does not take place. Many different materials may be used but it is preferred to employ those chelating agents that are disclosed in U.S. Pat. No. 3,838,102 (Bennett et al.).

The useful chelating agents include polyfunctional carboxylic acid containing compounds such as, for example, sodium potassium tartrate, nitrilotriacetic acid (NTA), citric acid, glycine and especially preferably they will be selected from polyalkylenepolyamine polycarboxylic acids, aminopolycarboxylic acids, aminocarboxylic acids, aminopolycarboxylic acids, aminocarboxylic acids, polycarboxylic acids and their alkali metal, alkaline earth metal or mixed alkali metal-alkaline earth metal salts. The preferred agents include ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid and their salts. Especially preferred are ethylenediaminetetraacetic acid or a mono-, di-, tri- and tetrasodium salt thereof and the resulting copper complex can be referred to as a copper carboxylate complex.

The chelated metallic catalyst component can be extracted with the water produced in the polymerization reaction by through the use of a liquid/liquid centrifuge. The preferred extraction liquid for use in the process of the invention is an aqueous solution of lower alkanol, i.e., a mixture of water and an alkanol having from 1 to about 4 carbon atoms. Generally from about 1% to about 80% by volume of an alkanol or glycol may be employed. These ratios may vary from about 0.01:1 to about 10:1 parts by volume of aqueous liquid extractant to discrete organic phase.

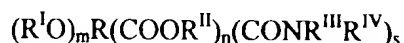
The reaction media generally comprises an aqueous environment. Anti-solvents can also be utilized in combination with the aqueous media to help drive the precipitation of the copper (I) species. The selection of an appropriate anti-solvent is based partially on the solubility co-efficient of the copper (I) species that is being precipitated. The halides are highly insoluble in water, $\log K_{[sp]}$ values at 25°C. are - 4.49, - 8.23 and - 11.96 for CuCl, CuBr and CuI, respectively. Solubility in water is increased by the presence of excess of halide ions due to the formation of, e.g., CuCl₂, CuCl₃, and CuCl₄ and by other complexing species. Non-limiting examples of anti-solvents would comprise low molecular weight alkyl and aromatic hydrocarbons, ketones, alcohols and the like which in themselves would have some solubility in the aqueous solution. One skilled in the art would be able to select an appropriate type and amount of anti-solvent, if any was utilized.

After removal of the catalyst, the PPE containing solution is concentrated to a higher solids level as part of the isolation of the PPE. The PPE can be readily functionalized prior to and/or during this solvent removal process by addition of at least one functionalizing agent, also known as compatibilizers or functionalizers. The location of the addition of at least one functionalizing agent will depend on several factors such as the stability of the agent, the volatility of the agent to the isolation conditions, the flexibility of the equipment for addition points, and the like. For functionalizing agents that are volatile in the isolation process, addition of the functionalizing agent prior to solvent removal is often preferred so as not to remove

functionalizing agents, greater flexibility in the location of the addition is possible. It is also possible to add functionalizing agent at several points during the process.

In one embodiment, the functionalizing agent includes compounds having both (i) a carbon-carbon double bond or a carbon-carbon triple bond and (ii) at least one species of the group consisting of carboxylic acids, acid anhydrides, acid amides, acid esters, imides, amines, ortho esters, hydroxyls and carboxylic acid ammonium salts. Illustrative compounds useful to accomplish the functionalization of the PPE include maleic anhydride, fumaric acid, maleimides such as N-phenylmaleimide and 1,4-phenylene-bis-methylene- α , α '-bismaleimide, maleic hydrazide, methyl nadic anhydride, fatty oils (e.g., soybean oil, tung oil, linseed oil, sesame oil), acrylate ortho esters and methacrylate ortho esters, unsaturated carboxylic acids such as acrylic, crotonic, methacrylic acid and oleic acid, unsaturated alcohols such as allyl alcohol and crotyl alcohol and unsaturated amines such as allylamine and trialkyl amine salts of unsaturated acids such as triethylammonium fumarate and tri-n-butylammonium fumarate. Examples of such typical reagents for preparing useful functionalized PPE are described in U.S. Pat. Nos. 4,315,086, 4,755,566, 4,888,397, and 5,247,006. In addition to unsaturated compounds, saturated anhydrides and esters are also useful for PPE functionalization presumably via capping the hydroxyl end groups. The functionalization may be accomplished in the melt or in an appropriate solvent. Examples of useful compounds include N-benzoyl-N-methylacetamid, N-acetyl- ϵ -caprolactam, N-benzoyl- ϵ -caprolactam, N-benzoyllauryllactam etc, as disclosed in the EP 0436802 A2. Other saturated compounds suitable for PPE end group modification are derivatives of malonic acid as described in DE 4018548 A1.

Non-polymeric aliphatic polycarboxylic acids are also useful for preparing functionalized PPE. Included in the group of species, are, for example, the aliphatic polycarboxylic acids, and acid esters represented by the formula:



wherein R is a linear or branched chain, saturated aliphatic hydrocarbon of from 2 to 20, preferably 2 to 10, carbon atoms; R^I is selected from the group consisting of hydrogen or an alkyl, aryl, acyl, or carbonyl dioxy group of 1 to 10, preferably 1 to 6, most preferably 1 to 4, carbon atoms, with hydrogen being especially preferred; each R^{II} is independently selected from the group consisting of hydrogen or an alkyl or aryl group of from 1 to 20 carbon atoms preferably from 1 to 10 carbon atoms; each R^{III} and R^{IV} is independently selected from the group consisting essentially of hydrogen or an alkyl or aryl group of from 1 to 10, preferably from 1 to 6, most preferably 1 to 4, carbon atoms; m is equal to 1 and (n + s) is greater than or equal to 2, preferably equal to 2 or 3, and n and s are each greater than or equal to zero; and wherein (OR^I) is alpha or beta to a carbonyl group and at least two carbonyl groups are separated by 2 to 6 carbon atoms. Obviously, R^I, R^{II}, R^{III} and R^{IV} cannot be aryl when the respective substituent has less than 6 carbon atoms.

Illustrative of suitable polycarboxylic acids are citric acid, malic acid, and agaricic acid; including the various commercial forms thereof, such as, for example, the anhydrous and hydrated acids. Illustrative acid esters useful herein include, for example, acetyl citrate and mono- and/or di-stearyl citrates and the like. Suitable acid amides useful herein include, for example, N,N'-diethyl citric acid amide; N,N'-dipropyl citric acid amide; N-phenyl citric acid amide; N-dodecyl citric acid amide; N,N'-didodecyl citric acid amide and N-dodecyl malic acid amide. Derivatives of the foregoing polycarboxylic acids are also suitable for use in the practice of the present invention. Examples of suitable functionalizing compounds can be found in U.S. Pat. Nos. 4,315,086, 4,755,566, 4,873,286 and 5,000,897.

[illegible]

acetyl-3,4-dibenzoic acid anhydride, terephthalic acid acid chloride, and reactive triazines including epoxyalkyl chlorocyanurates and chloroaryloxytriazines. Additional examples can be found in U.S. Pat. Nos. 4,600,741 and 4,642,358. One unexpected benefit of the low I.V. PPE is the increased solubility in a wider range of solvents, especially at lower temperatures. For example, PPE having an I.V. of greater than about 0.35 dl/g are only marginally soluble in tetrahydrofuran (THF), however, low I.V. PPE are readily soluble even at fairly high concentration levels. The increased solubility affords wide ranging advantages and flexibility in many commercial applications.

The amount of the above mentioned functionalizing agents that is required to appropriately functionalize the PPE is that which is sufficient to improve the compatibility between the various components in the final composition. As previously discussed, indications of improved compatibility include resistance to lamination, improved physical properties such as increased tensile and impact properties and a stabilized morphology between the blend component phases under static or low shear conditions. One unexpected advantage of the low I.V. PPE is the higher level of phenolic endgroups affords the possibility of higher levels of functionality, especially with endgroup reactive functionalizing agents. Moreover, the higher level of phenolic endgroups increases the utilization efficiency of the functionalizing agent.

An effective amount of the above mentioned functionalizers, based on the amount of the PPE, is generally up to about 8% by weight, and is preferably from about 0.05% to about 4% by weight. In the most preferred embodiments, the amount of functionalizing agent is in the range of about 0.1% to about 2.0% by weight based on the amount of the PPE. The actual amount utilized will also depend on the molecular weight of the functionalizing agent, the number and type of reactive species per molecule of functionalizing agent and the degree of compatibility that is desired in the final resin blend composition.

Depending on the target I.V. desired for the compositions, various techniques for isolating the PPE are useful. When the final I.V. of the PPE to be utilized is greater than about 0.28 dl/g, standard solvent based techniques, e.g., precipitation of the PPE containing reaction solution into a non-solvent followed by collection and drying of the PPE are useful. Conversely, using standard non-solvent techniques typical for PPE having I.V.'s greater than 0.28 dl/g are not generally useful for isolation of lower molecular weight PPE due to the small PPE particle size and friability of the particles. Very low yields are often obtained with undesirable fractionation of oligomeric species. A total isolation process is preferred for isolating the PPE. As part of the total isolation, a portion of the solvent is preferably removed in order to reduce the solvent load on the total isolation equipment.

Concentration of the PPE containing solution is accomplished by reducing the pressure in a solvent flash vessel while preferably increasing the temperature of the PPE containing solution. Pressures of about 35 to 50 bar are desirable with solution temperatures increased to at least 200°C, preferably of at least 230°C. A solids level of PPE of at least 55%, preferably of at least 65% or higher is desirable.

The isolation of the PPE is typically carried out in a devolatilizing extruder although other methods involving spray drying, wiped film evaporators, flake evaporators, and flash vessels with melt pumps, including various combinations involving these methods are also useful and in some instances preferred. As previously described, total isolation is preferably from the viewpoint that oligomeric species are not removed to the same degree as with precipitation. Likewise, isolation yields are extremely high and are near quantitative. These techniques require however that the catalyst removal be completed in the prior process steps as any catalyst remaining in solution will necessarily be isolated in the PPE.

Devolatilizing extruders and processes are known in the art and typically involve a twin-screw extruder equipped with multiple venting sections for solvent removal. In the practice of the present invention, it is preferred when isolating PPE

having an I.V. of about 0.28 or less that the preheated concentrated solution containing the PPE be fed into the devolatilizing extruder and maintained at a temperature less than about 275°C, and preferably less than about 250°C, and most preferably between about 185-220°C with pressures in the vacuum vent of less than about 1 bar. The resultant solvent level is reduced to less than about 1200 ppm, preferably less than about 600 ppm, and most preferably less than about 400 ppm. The styrenic block copolymer may optionally be added, at least in part, into the devolatilizing extruder to prepare either a concentrate or the final composition. An advantage of this is the possible elimination of a subsequent mixing/compounding step

Another advantage of using a devolatilizing extruder is the extremely high yield of PPE achieved in the process. For example, a PPE yield of over 99% have been obtained even for PPE having a low I.V. whereas in the precipitation process known in the art, the yield of similar low I.V. PPE was less than 90%. Thus, the present process preferably comprises PPE obtained through a devolatilization process to remove the solvent. A devolatilizing extruder typically affords a method to prepare low molecular weight polyphenylene ether resin, typically within the intrinsic viscosity range of about 0.08 dl/g to about 0.20 dl/g, in a yield of over 90%, preferably over 95%, more preferably over 98% and most preferably over 99%, based upon the amount of monovalent phenol utilized in the oxidative coupling.

When using a devolatilization extruder for the total isolation of the PPE, traditional underwater or water spray cooling of strands of extrudate followed by chopping the extrudate into pellets often gives unacceptable results presumably due to the low melt strength and inherent brittle nature of low molecular weight PPE. It was found that special pelletization techniques can overcome these difficulties. Useful techniques include die-face pelletization, including underwater pelletization and flaking, declining angle strand pelletization using water spraying, and vibration drop pelletization with underwater pelletization especially suitable.

Underwater pelletization also results in a significantly lower color in the PPE as compared to the standard stranding with water/air cooling followed by pelletization techniques. Yellowness index (YI) numbers of less than 30, and even less than 25 are achievable as compared to $YI > 50$ achieved with the standard stranding technique. It should be apparent that the present invention includes compositions comprising (i) at least one styrenic block copolymer and (ii) at least one polyphenylene ether resin having an intrinsic viscosity within the range of about 0.05 dl/g to about 0.60 dl/g, preferably within the range of about 0.08 dl/g to about 0.20 dl/g, as measured in chloroform at 25°C. wherein the PPE was made by a process that affords a method of preparing a PPE with a YI of less than about 30, preferably less than about 25.

Another unexpected benefit of underwater pelletization of PPE, especially low I.V. PPE, is that very low (less than about 3% by weight) fines, defined as pellets (i.e. particles) of less than 850 microns in size, could be obtained. It should be clear that the present invention includes a method to reduce the number of fines having a particle size less than about 850 micron in polyphenylene ether wherein the method comprises underwater pelletization of the polyphenylene ether resin. A preferred embodiment includes a method to prepare the compositions of the invention wherein the method comprises reducing the number of PPE fines having a particle size less than about 850 micron to less than about 3%, preferably less than about 1.5% by weight based on the total weight of the pellets and mixing the PPE with at least one styrenic block copolymer.

The compositions of the present invention can be prepared by a variety of methods involving intimate admixing of the materials with any additional additives desired in the formulation. Suitable procedures include solution blending and melt blending. Because of the availability of melt blending equipment in commercial polymer processing facilities, melt processing procedures are generally preferred. Examples of equipment used in such melt compounding methods include: co-rotating and counter-rotating extruders, single screw extruders, disc-pack processors and

material exits the extruder through small exit holes in a die and the resulting strands of molten resin are cooled by passing the strands through a water bath. The cooled strands can be chopped into small pellets for packaging and further handling.

All of the ingredients may be added initially to the processing system, or else certain additives may be pre-compounded with each other. It is also sometimes advantageous to employ at least one vent port in each section between the feed ports to allow venting (either atmospheric or vacuum) of the melt. Those of ordinary skill in the art will be able to adjust blending times and temperatures, as well as component addition location and sequence, without undue additional experimentation. Additionally, concentrates containing relatively high levels of PPE in the styrenic block copolymer may be used that are let down to the desired lower level of PPE with additional styrenic block copolymer by, for example, a converter manufacturing sheet products or articles are also contemplated. By relatively high level of PPE is meant a concentrate that contains at least 20%, preferably at least 30% by weight, more preferably at least 40% by weight PPE based on the weight of the concentrate. Such concentrates may be primarily composed of the polyphenylene ether resin and the styrenic block copolymer or may be composed of another resin such as, for example, a polystyrene resin. The concentrate may also contain one or more of the additives and/or stabilizers as follows.

Additives such as antioxidants (e.g., hindered phenols such as, for example, IRGANOX Registered TM 1010), phosphites (e.g., IRGAFOS Registered TM 168)), U.V. stabilizers, cling additives (e.g., polyisobutylene), antiblock additives, colorants, pigments, fillers, carbon fibers, carbon fibrils, and the like can also be included in the compositions of the present invention, to the extent that they do not interfere with the enhanced properties of the compositions.

The additives are employed in functionally equivalent amounts known to those skilled in the art. For example, the amount of antioxidant employed is that amount which prevents the polymer from undergoing oxidation at the temperatures

and environment employed during storage and ultimate use of the polymers. Such amounts of antioxidants is usually in the range of from about 0.01 to about 10, preferably from about 0.05 to about 5, more preferably from about 0.1 to about 2 percent by weight based upon the weight of the polymer.

Similarly, the amounts of any of the other enumerated additives are the functionally equivalent amounts such as the amount to render the polymer antiblocking, to produce the desired amount of filler loading to produce the desired result, to provide the desired color from the colorant or pigment. Such additives can suitably be employed in the range of from about 0.05 to about 50, preferably from about 0.1 to about 35 more preferably from about 0.2 to about 20 percent by weight based upon the total weight of the polymers. However, in the instance of fillers, they could be employed up to about 90 percent by weight based on the total weight of the polymers.

The compositions of the present invention can be utilized to produce a wide range of fabricated articles such as, for example but not limited to, films, sheets or as a components of a multilayered structure resulting from calendering, blowing, casting or (co-)extrusion operations.

The compositions can find utility in the form of fabricated articles produced, for example, by rotation molding, compression molding, injection molding, blow molding, calendering, sheet extrusion, profile extrusion, or thermoforming operations.

The compositions can also be used in the manufacture of fibers, foams and lattices. The compositions of the present invention can also be utilized in adhesives, adhesive formulations and adhesive/sealant applications. There is very broad range of applications for the compositions of the invention, including: automotive, consumer, industrial/mechanical, sheet and profile, tires, medical, wire and cable coatings, asphalt modifiers for roofing and paving materials, footwear, lubricating oils, packaging films, business machines, automotive body panels, tires, sound deadening

and vibration dampening materials for automotive, high temperature labels and tapes, sealants and caulks, glazing, and construction materials, and the like.

It should be clear that in some preferred embodiments, the compositions of the present invention are substantially free of other thermoplastic resins. The other thermoplastic resins that the compositions should be substantially free of include polyamide resins, polysiloxanes, ABS, polyvinyl chloride, polyurethanes, thermoplastic elastomers, polyarylene sulfides, polystyrene resins, high impact polystyrene resins, polyester resins, polycarbonate resins, polysulfone resins, polyarylate resins, polyphenylene sulfide resins, and polyetherimide resins as well as various mixtures of other thermoplastic resins. By "substantially free" is meant that the compositions contain less than 5% by weight, preferably less than 3% by weight, more preferably less than 1% by weight, and most preferable essentially none of the other thermoplastic resins, wherein all percentages by weight are based upon the entire weight of the composition.

The thermoplastic composition of the invention may comprise any of the following additives: stabilizers, dyes, fillers, reinforcing agents, minerals, flame retardants, carbon fibers, carbon fibrils, and pigments.

A suitable level of the various components depends on several factors, such as the end-use of the product, the level of various properties desired, and the particular type and characteristics of other components which are present. Although the present invention includes compositions containing from 1 to 99% by weight of the present PPE and from 99 to 1% by weight of the styrenic block copolymer, in some embodiments, the level of the PPE is from about 1 to about 60% by weight based on the weight of the entire composition. In another embodiment, the PPE is present in an amount of from 1 to about 40% by weight, preferably from about 1 to about 35% by weight.

Preparation of the compositions of the present invention is normally achieved by solution blending in a solvent or melt blending the ingredients under conditions for

the formation of an intimate blend. One unexpected advantage of the present invention is the increased solubility of the present low I.V. PPE in a wide variety of solvents, thus expanding the manufacturing options. Melt conditions often include mixing in single or twin screw type extruders or similar mixing devices that can apply a shear to the components. It is often advantageous to apply a vacuum to the melt through a vent port in the extruder to remove volatile impurities in the composition.

All of the ingredients may be added initially to the processing system, or else certain additives may be pre-compounded with each other or with one of the primary polymer components, PPE and/or styrenic block copolymer. It appears that certain properties, such as tensile strength and elongation, are sometimes enhanced by initially functionalizing the PPE with at least some of the styrenic block copolymer to form a concentrate of the PPE in the styrenic block copolymer followed by letting down the concentrate with additional styrenic block copolymer resin. While separate extruders may be used in the processing, these compositions may also be prepared by using a single devolatilizing extruder having multiple feed ports along its length to accommodate the addition of the various components. It is also sometimes advantageous to employ at least one vent port in each section between the feed ports to allow additional venting (preferably vacuum) of the melt. Those of ordinary skill in the art will be able to adjust blending times and temperatures, as well as component addition location and sequence, without undue additional experimentation.

All patents and references cited by reference are incorporated herein by reference.

Examples

The following examples are illustrative of specific embodiments of the invention and are not to be construed as limiting the scope of the invention.

A twin-screw extruder or a single screw extruder may be utilized to melt compound the PPE with the styrenic block copolymer. It is important to control the

temperature and shear of the molten compositions so as to minimize the degradation of the styrenic block copolymer. Concentrates of PPE and another material, preferably styrenic block copolymer, may also be used directly in calendering, injection molding, blowing, casting, or (co)extrusion operations. Alternatively, the PPE and the styrenic block copolymer may be mixed in a common solvent or mixed solvent system depending on the exact application requirements.

Better compatibility between the PPE and styrenic block copolymers can be obtained with the low molecular weight (i.e. low I.V.) PPE of the present invention as compared to PPE having an I.V. of greater than about 0.35 dl/g of the prior art. By better compatibility is meant reduced delamination tendencies and enhanced physical properties such as, for example, tensile strength and tensile elongation. It is unexpected that low molecular weight PPE can be combined with styrenic block copolymers to achieve a composition having an acceptable level of compatibility based upon the prior art teachings of the necessity to having high molecular weight polymer. Additionally, the low I.V. of the present invention results in more clear, i.e. translucent, blends with styrenic block copolymer than does PPE with high intrinsic viscosities of the prior art.

Changes in the PPE I.V. also affects the physical properties of the composition with improved compatibility between the PPE and the styrenic block copolymer generally obtained with PPE having an I.V. less than about 0.3 dl/g, preferably less than about 0.2 dl/g, and most preferably less than about 0.15 dl/g. It should be clear that the present invention includes a method for improving the compatibility between PPE and a styrenic block copolymer wherein the method comprises at least one of varying the molecular weight of the PPE and/or varying the weight ratio of the styrenic block copolymer and PPE.

Addition of PPE to the styrenic block copolymer improves the heat resistance of the styrenic block copolymer as well as altering the rheological characteristics. For example, styrenic block copolymers may be used as viscosity index improvers and

may be added to motor lubricating oils to improve the temperature - viscosity relationship. Adding the low molecular weight PPE of the present invention can result in modified temperature viscosity relationships. Moreover, addition of low molecular weight PPE to styrenic block copolymer resins affords a method to tailor the hardness/softness of the compositions. This method is useful in applications such as, for example, footwear, golf club handles, automotive sealants, food dispensing tubes and the like. Additionally, improved elevated compression set capability and abrasion resistance as well as enhanced heat resistance are additional benefits.

Styrenic block copolymers may be used as coatings in wire and cable industry. The use of the low molecular weight PPE of the present invention may help improve the thermal performance of such coatings.

Styrenic block copolymers can be used for packaging films. Addition of the low molecular weight PPE of the present invention may result in improvements in thermal performance.

Addition of the low molecular weight PPE of the present invention to styrenic block copolymers may help improve their thermal performance in applications where styrenic block copolymers are used to increase the impact strength and stress crack resistance of polymers such as polyethylene, polypropylene, polystyrene and engineering thermoplastics.

Styrenic block copolymers are also added to control shrinkage in polyester resins and the addition of the low molecular weight PPE of the present invention may improve thermal performance.

Styrenic block copolymers may be used for automotive body panel applications. These materials, however, lack in higher temperature performance. Addition of the low molecular weight PPE of the present invention may help improve the high temperature performance of these systems.

Styrenic block copolymers are also useful in asphalt modification: The performance of asphalt in roofing and paving applications may be significantly improved by the addition of 3-10% polystyrene-polybutadiene-polystyrene block copolymers. At low concentrations, the blend is an asphalt modified by a polymer, while at higher concentrations an interconnecting polymer network is formed and the blend becomes a polymer extended by asphalt. The block copolymer makes the blend more flexible at low temperature and reduce the tendency to flow at high temperatures. This makes the blend easier to apply and increases the tensile strength, ductility and elastic recovery of the final product. A large advantage of the low molecular weight PPE of the present invention over the high molecular weight PPE of the art is that presumably due to its smaller size, this low molecular weight PPE can better penetrate the styrenic domains of styrenic block copolymers. Within modified bitumen systems, styrenic block copolymer are increasing in use as the price of atactic polypropylene resins, the major bitumen modifier has decreased.

Styrenic block copolymers are also used in road repair and paving materials. Addition of the low molecular weight PPE of the present invention can help improve thermal performance.

Addition of the low molecular weight PPE of the present invention to styrenic block copolymers for their use in pressure sensitive adhesives, sealants and hot melt adhesives may afford the opportunity to increase the thermal performance of these resins.

Addition of the low molecular weight PPE of the present invention to styrene-butadiene elastomers may help improve the thermal performance of the materials, especially in their use in tires.

CLAIMS:

What is claimed:

1. A composition comprising:
 - a) at least one styrenic block copolymer resin; and
 - b) at least one polyphenylene ether resin.
2. The composition of Claim 1 wherein the composition is substantially free of other thermoplastic resins.
3. The composition of Claim 1 wherein the composition is substantially free of thermoplastic resins of the group consisting of polyamide resins, polysiloxanes, ABS, polyvinyl chloride, polyurethanes, polyarylene sulfides, polystyrene resins, high impact polystyrene resins, polyolefin resins, polyester resins, polycarbonate resins, polysulfone resins, polyethersulfone resins, polyarylate resins, polyphenylene sulfide resins, polyetherimide resins, and mixtures containing at least one of the foregoing.
4. The composition of Claim 1 wherein the polyphenylene ether resin has an intrinsic viscosity within the range of about 0.08 dl/g to about 0.20 dl/g as measured in chloroform at 25°C.
5. The composition of Claim 1 wherein the polyphenylene ether resin is present in an amount up to about 50% by weight based upon the weight of the composition.
6. The composition of Claim 1 wherein the polyphenylene ether resin is present in an amount up to about 20% by weight based upon the weight of the composition.
7. The composition of Claim 1 wherein the polyphenylene ether resin is made by a process comprising oxidative coupling in a reaction solution at least one monovalent phenol species using an oxygen containing gas and a complex metal catalyst to produce a polyphenylene ether resin having an intrinsic viscosity within the range of

about 0.05 dl/g to about 0.60 dl/g as measured in chloroform at 25°C; recovering the complex metal catalyst with an aqueous containing solution and isolating the polyphenylene ether resin through devolatilization of the reaction solvent.

8. The composition of Claim 7 wherein the process produces a polyphenylene ether resin having an intrinsic viscosity within the range of about 0.08 dl/g to about 0.20 dl/g as measured in chloroform at 25°C.

9. The composition of Claim 7 wherein the process further comprises an equilibration of a metal chelating agent with the complex metal catalyst.

10. The composition of Claim 7 wherein the intrinsic viscosity of the polyphenylene ether resin after the equilibration has less than a 10% change in intrinsic viscosity as before the equilibration.

11. The composition of Claim 7 wherein the devolatilization is accomplished at least in part with a devolatilization extruder.

12. The composition of Claim 11 wherein the devolatilization extruder is at least partly operated at between about 185-220°C.

13. The composition of Claim 11 wherein the reaction solvent has a solids level of at least about 65% before feeding into the devolatilization extruder.

14. The composition of Claim 7 wherein the polyphenylene ether resin has less than about a 10% drop in intrinsic viscosity after an equilibration step following the oxidative coupling.

15. The composition of Claim 7 wherein the polyphenylene ether resin has less than about a 10% change in intrinsic viscosity after an equilibration step following the oxidative coupling and after a thermal treatment at 200°C for about 0.2 minutes to about 20 minutes.

16. The composition of Claim 7 wherein the monovalent phenol species comprises 2,6-dimethylphenol or a mixture of 2,6-dimethylphenol and 2,3,6-trimethylphenol.

17. The composition of Claim 7 wherein the polyphenylene ether resin has an incorporated amine content of less than about 0.3% by weight based on the weight of the polyphenylene ether resin.

18. The composition of Claim 7 wherein the devolatilization is accomplished at least in part with a devolatilization extruder and an underwater pelletizer.

19. The composition of Claim 7 wherein the polyphenylene ether resin has a residual volatiles level of less than about 600 ppm based on the weight of the polyphenylene ether resin.

20. The composition of Claim 1 wherein the polyphenylene ether resin comprises a polyphenylene ether resin that has an incorporated amine content of less than about 0.3% by weight based on the weight of the polyphenylene ether resin.

21. The composition of claim 1 wherein less than about 50% of the poly(phenylene ether) has two hydroxyl groups per polymer chain.

22. The composition of claim 1 wherein less than about 25% of the poly(phenylene ether) has two hydroxyl groups per polymer chain.

23. The composition of claim 1 wherein less than about 10% of the poly(phenylene ether) has two hydroxyl groups per polymer chain.

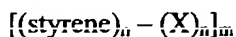
24. The composition of Claim 1 wherein the polyphenylene ether resin is made from at least 2,6-dimethylphenol or a mixture of 2,6-dimethylphenol and 2,3,6-trimethylphenol.

25. The composition of Claim 1 wherein the polyphenylene ether resin comprises a functionalized polyphenylene ether resin.

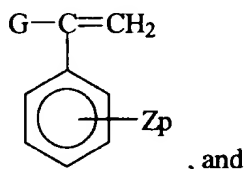
26. The composition of Claim 1 wherein the polyphenylene ether resin comprises a functionalized polyphenylene ether resin made through redistribution of a functionalized phenolic compound.

27. The composition of Claim 1 wherein the styrenic block copolymer resin comprises a poly(alkenylaromatic) block of at least about 15 repeat units attached to a second polymer or copolymer of at least about 15 repeat units.

28. The composition of Claim 1 wherein the styrenic block copolymer resin comprises copolymers represented by the general formula:



wherein styrene is an alkenylaromatic monomer of the formula:



wherein G is hydrogen, lower alkyl, or halogen; Z is vinyl, halogen, or lower alkyl; and p is from 0 to 5, and wherein X is a second polymer or copolymer of one or more monomers, n is at least 15 and m is at least 1.

29. The composition of Claim 25 wherein X can be selected from the group consisting of polyesters, polyamides, polyolefins, polycarbonates, polyimides, polysulfones, polyethersulfones, polyphenylene ethers, liquid crystalline polymers, as well as copolymers containing at least one of the foregoing, and the like.

30. The composition of Claim 1 wherein the styrenic block copolymer resin is a block copolymer, graft copolymer, or a combination of a block copolymer and graft copolymer.

31. The composition of Claim 1 wherein the styrenic block copolymer resin is a di-block copolymer, tri-block copolymer, or higher multi-block copolymer, branched copolymer, multi-arm copolymer, radial copolymer, comb copolymer, tapered copolymer, or a combination of the foregoing.

32. The composition of Claim 1 wherein the styrenic block copolymer resin is at least one elastomeric block copolymer resins of the group consisting of polystyrene-poly(ethylene-butylene), polystyrene-polyisoprene, poly(α -methylstyrene)-polybutadiene-poly(α -methylstyrene), polystyrene-poly(butadiene), polystyrene-poly(butadiene)-polystyrene block copolymers, poly(α -methylstyrene)-polybutadiene, polystyrene-poly(ethylenebutylene)-polystyrene block copolymers and polystyrene-poly(ethylenepropylene) block copolymers.

33. A fabricated article comprising the composition of Claim 1.

34. The fabricated article made of Claim 33 wherein the fabricated article is made by at least one of compression molding, injection molding, blow molding, profile extrusion, or thermoforming operations.

35. A fiber, foam, or latice comprising the composition of Claim 1.

36. An adhesive formulation comprising the composition of Claim 1.

37. A composition consisting essentially of:

- a) at least one styrenic block copolymer resin; and
- b) at least one polyphenylene ether resin, wherein the polyphenylene ether resin has an intrinsic viscosity within the range of about 0.08 dl/g to about 0.20 dl/g as measured in chloroform at 25°C..

38. The composition of Claim 37 wherein the composition is free of other thermoplastic resins.

39. The composition of Claim 37 wherein the composition is free of thermoplastic resins of the group consisting of polyamide resins, polysiloxanes, ABS, polyvinyl chloride, polyurethanes, polyarylene sulfides, polystyrene resins, high impact polystyrene resins, polyolefin resins, polyester resins, polycarbonate resins, polysulfone resins, polyethersulfone resins, polyarylate resins, polyphenylene sulfide resins, polyetherimide resins, and mixtures containing at least one of the foregoing.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/08778

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L53/02 C09J153/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 732 370 A (GEN ELECTRIC) 18 September 1996 (1996-09-18) * page 2, line 35 - page 3, line 21 ; claims 11, 1, 7, 8, 10 ; page 7, line 20-38 ; page 3, line 29 - page 4, line 11 ; examples ; page 7, line 55 - page 8, line 21 ; claims 1-21 ; page 8, line 29-34 * page 7, line 46-50	1-35, 37-39
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Y	* page 2, line 35 - page 3, line 30 ; page 3, line 52 - page 4, line 26 ; claims 2, 6-9 * page 5, line 41-51	35
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/08778

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